PATENT SPECIFICATION (11) 1271463

1271463

DRAWINGS ATTACHED

(21) Application No. 56217/69 (22) Filed 17 Nov. 1969

(31) Convention Application No. 820267 (32) Filed 29 April 1969 in

(33) United States of America (US)

(45) Complete Specification published 19 April 1972

(51) International Classification B 01 j 13/02

(52) Index at acceptance

B8C A

B2E 185 18Y 19Y 204 206 207 20Y 299 319 339 349 368 380 382 383 384 385 386 387 38X 38Y 390 392 393 39X 39Y 409 412 419 41X 41Y 420 422 424 42X 42Y 435 43Y 447 44Y 457 462 463 464 473 485 486 487 495 49Y 515 517 52Y 536 543 54Y 555 55Y 563 570 575 576 577 57Y 58Y

(54) MICROCAPSULAR OPACIFIERS AND PROCESS FOR THEIR MANUFACTURE

(71) We, THE CHAMPION PAPER COMPANY, LTD., a corporation of Switzerland, of Alpenstrasse 1, Lucerne, Switzerland, do hereby declare the invention for which we pray that a patent may be granted to us and the method by which it is performed to be particularly described in and by the following statement:—

This invention relates to a method for providing high opacity in fibrous and non-fibrous substrates, surface finishes and to the substrates produced by such method. More specifically, it relates to pigmented microcapsular opacifiers, to their production, and to their use in coatings, substrates and the like.

The development of fibrous and non-fibrous systems having a high opacity has always been a great concern to paper manufacturers and paint manufacturers.

The degree of opacity of a particular substrate is the result of diffuse light-scattering which occurs when visible radiation is reflected from particles on the surface of the substrate and in the substrate medium itself. It has been conventional to employ coatings of high density inorganic fillers, such as titanium dioxide, calcium carbonate and certain clays, to enhance the opacity of various substrates. However, the employment of such fillers has many disadvantages in the production of paper, for example.

Generally, the use of such inorganic opacifying materials greatly increases the weight of the paper. This increase in weight is not consistent with the increasing market demands for producing a lighter-weight paper having high opacity.

Also, the incorporation of large amounts of fillers in paper results in a substantial loss of the paper web strength. In addition, the generally low retention of the inorganic opacifiers in the paper results in a substantial monetary loss by virtue of the high by-product waste material thereby resulting. More importantly, this results in heavy contamination of streams and other waterways. In addition to the foregoing disadvantages in the employment of such inorganic filler materials in paper, most inorganic fillers possess a low opacity-to-weight ratio when incorporated in paper and other thin substrates.

For about the last ten years, microcapsules containing both liquid and solid nucleus materials have found acceptance in a variety of commercial applications. For example, one of the most widespread uses of microcapsules has been in the art of transfer-copy systems. Other recent applications in which the microcapsules have been used extensively are in adhesives and adhesive tapes, fertilizers, pharmaceuticals, foods and cosmetics.

In our co-pending Application No. 46612/69 Serial No. 1270408) we have described and claimed discrete substantially spherical air-filled microcapsules having substantially continuous organic polymeric solid walls, said microcapsules having an average diameter not substantially greater than 1.0 micron. It was found that when such air-containing microcapsules were coated onto and/or incorporated into a substrate, such as paper, glass, film, metal or wood or incorporated into surface finishes such as paints, they significantly increased the opacity of the substrate by scattering back substantial amounts of the incident light which would otherwise be transmitted by the substrate. Furthermore, it was discovered that when such air-containing microcapsules were incorporated into and onto various substrates, high opacities result which were heretofore unobtainable with similar amounts of inorganic opacifiers. Since the air-containing microcapsules were relatively light in weight, the incorporation of such micro-

capsules into a fibrous cellulosic substrate, for example, induced a high opacity for the substrate, without greatly increasing the weight of the substrate.

It is an object of this invention to provide a means for increasing the opacity of fibrous and non-fibrous substrates, without significantly increasing the weight of said substrates, to an extent not heretofore possible.

It is another object of this invention substantially to improve the optical properties, e.g., opacity and brightness, of fibrous substrates without decreasing the web strength of such substrate.

Another object of the present invention is to provide fibrous and non-fibrous substrates having an increased brightness without a substantial attendant increase in weight.

Still another object of the present invention is to provide opacifiers which possess a high opacity-to-weight ratio when incorporated into coatings, on fibrous and in non-fibrous substrates.

Another object of the present invention is to provide a method for the production of the light weight opacifiers possessing a high opacity-to-weight ratio.

The present invention provides discrete substantially spherical air-filled microcapsules having substantially continuous organic polymeric solid walls and an average particle diameter of less than 2 microns, said microcapsules also having inorganic pigment particles incorporated in the microcapsular structure.

The invention further provides a method for the production of such microcapsules which comprises preparing discrete, substantially spherical, precursor microcapsules pigmented with an inorganic pigment and having substantially continuous organic polymeric solid walls said microcapsules having an average diameter of less than 2 microns and containing a volatilisable liquid core material, and heating said microcapsules in the presence of air to a temperature sufficient to substantially completely volatilise said core material from said microcapsules and replace said core material by air.

It has been found that when a finely divided, inorganic opacifying pigment is incorporated into the microcapsular structure of the precursor microcapsules and the microcapsules are treated to introduce air into the core thereof, the resulting microcapsular opacifiers provide an increase in opacity not hitherto obtainable when they are incorporated into coatings, applied to fibrous substrates and incorporated into non-fibrous substrates. When the microcapsular opacifiers of the present invention are incorporated into fibrous substrates they do not interfere with interfiber bonding. On the contrary, they have been found actually to enhance interfiber bonding and act as "spot-welders" at points of contact between fibers. At the same time, the weight of such substrates is not substantially increased, since the microcapsule-containing pigment particle provides a greater increase in opacity than does the pigment particle, alone. As will be hereinafter demonstrated, the employment of the present microcapsular opacifiers as a coating for a paper substrate results in an increase in the opacity of the substrate which is substantially greater than the corresponding increase in opacity obtained with an equivalent amount of the inorganic pigment or air-containing microcapsules alone, respectively.

The microcapsular opacifiers of the present invention comprise discrete, essentially spherical microcapsules containing air and pigment particles. The microcapsules have substantially continuous, organic polymeric solid walls and an average particle diameter less than two microns. However, it is much preferable that the microcapsules have an average particle diameter below about one micron, while the range of between 0.25 and 0.8 micron is especially preferred in the practice of the present invention.

The term "substantially continuous solid walls" as employed herein is intended to include solid-walled microcapsules which are still sufficiently porous to permit the escape of vaporizable core material in gaseous form therethrough upon the application of heat. The core material passes through the micropores of the capsule and is replaced therein with air. The core materials that may be employed in the production of the present microcapsular opacifiers are more particularly defined hereinafter.

Any suitable inorganic pigment may be incorporated into the air-containing microcapsular opacifiers. Such pigments include those finely divided materials which have been conventionally employed for the purpose of increasing opacity of substrates, such as paper. Accordingly, suitable pigments include, for example, TiO_2, $CaCO_3$, $Al_2O_3 \cdot 3H_2O$, barytes ($BaSO_4$), clay, ZnO, ZnS, $CaSO_3$, $CaSiO_3$ and talc. Preferred inorganic pigments for the purpose of the present invention are TiO_2, $CaCO_3$, $Al_2O_3 \cdot 3H_2O$, $BaSO_4$, clay and ZnO, with TiO_2 being especially preferred.

Any desired pigment particle size may be employed, so long as it is suitable for incorporation into the microcapsular structure. Thus, for example, TiO_2 having a particle size of between 0.1 and 0.35 micron, is highly suitable for the purposes of the present invention. Other suitable exemplary pigment particle sizes for use in the present invention are set forth below:

Pigment	Average Particle Size (Microns)
ZnO	0.12
Barytes ($BaSO_4$)	0.25
$CaCO_3$	0.9
Clay (Ultrawhite 90)	2.0
Al_2O_3 Trihydrate	0.67

The microcapsular opacifiers of the present invention may be produced by a method which comprises preparing discrete, essentially spherical precursor microcapsules having substantially continuous organic polymeric solid walls, said microcapsules having an average diameter of less than 2 microns and containing pigment and a volatilisable core material, which is a liquid or low melting oil, fat or wax, or a water-miscible liquid, such as low molecular weight alcohol or ketone, and heating the microcapsules to a sufficient temperature, to substantially completely volatalise the core material from the microcapsules.

The precursor microcapsules of the present invention may be made in any suitable manner, so long as the walls of the capsules have sufficient structural integrity to permit the volatilisable core material to pass therethrough when heated without being ruptured or deformed into a substantially non-spherical shape. For example, precursor microcapsules may be prepared which have continuous organic polymeric solid walls of a hydrophobic resin and contain minute droplets of an oil-in-water emulsion. Likewise, continuous organic polymeric solid-walled, precursor microcapsules containing a water-immiscible oily material may be made by adding a cross-linking or complexing agent to an oil-in-water emulsion of which the continuous phase is a colloidal solution of one or more colloidal emulsifying agents, which emulsifying agent or agents possessses or possess a group or groups capable of reacting with a cross-linking or complexing agent.

Precursor oil-containing microcapsules may be produced by the technique known as "coacervation," which microcapsules can be employed for the production of the opacifiers of the present invention. Any microencapsulation method, whether chemical or physical, that is capable of yielding air-containing microcapsules containing inorganic pigment and having an average particle diameter of less than 2 microns may be employed.

As previously mentioned, precursor microcapsules may be provided which have substantially continuous organic polymeric solid walls of a hydrophobic resin and an average diameter of less than 2 microns and contain minute droplets of an oil-in-water emulsion. The process for providing such microcapsules comprises a simple admixing of inorganic pigment with at least four ingredients. These ingredients are:

(A) A water-immiscible oily material which is a liquid or low melting oil, fat or wax;

(B) an amphiphilic colloidal emulsifying agent having a group or groups capable of reacting with a crosslinking or complexing agent and which subsequently becomes incorporated into the wall structure of the precursor microcapsules;

(C) at least one solution comprising a resinous polymer, said solution being either

(1) a solution comprising a hydrophobic, thermoplastic resinous polymer which is substantially insoluble in said oil, fat or wax dissolved in a water-and oil-miscible organic solvent, said thermoplastic plastic polymer being capable of being separated from said solution in solid particulate form upon dilution with water or

(2) a solution comprising a partially condensed thermosetting resinous polymer in water, said polymer being capable of separating from said solution upon dilution with more water, and

(3) mixtures of (1) and (2), and,

(D) sufficient additional water to cause the separation of said thermoplastic polymer and/or said thermosetting resinous polymer from solution (1) or solution (2).

The inorganic pigment of suitable particle size may be incorporated into the microcapsular structure in any suitable manner. For example, it may be admixed with the oily material (A), an aqueous solution of the emulsifying agent (B), the resinous polymer solution (C), or may be supplied via any or all of the foregoing. Desirable results are obtainable regardless of the method of addition of pigment used.

The sequence of admixing of ingredients must be such that said thermoplastic and/or thermosetting polymer separates in solid form interface of oil-in-water droplets newly or previously formed and upon gradual addition of said additional water under conditions of brisk agitation. In other words, dilution with water, which can be performed by the addition of water to the oil-emulsifier-resin solution admixture or by the addition of the resin solution to the water-oil-emulsifier admixture, must be the final operation of the precursor microcapsule-forming process. In the one case, the emulsifying operation and the encapsulation operation can be considered to take place simultaneously, whereas, in the other case, the emulsion is already formed when it is admixed with the resin solution.

Although it is not intended to limit the present invention by any particular theory, it is postulated that the inorganic pigment particles

may have some, although weak, emulsifying properties. Thus, the pigment particles may tend to go to the interface of the emulsion droplets rather than remain dispersed in the oil phase upon encapsulation. Thus, when encapsulation of the oily droplets takes place, the pigment particles become incorporated in the microcapsular structure at a point depending upon its position after the emulsification step, e.g., at the emulsion droplet interface or in the interior of the emulsion droplet. For example, the pigment particles may be completely encapsulated within the walls of the microcapsules, or they may protrude through the microcapsular walls. Accordingly, it will be understood that when the specification refers to the microcapsules as "containing" the inorganic pigment, it is intended to include microcapsules having at least a portion of the inorganic pigment particle incorporated in the microcapsular structure. Likewise, the term "pigmented microcapsule" refers to microcapsules having at least a portion of the inorganic pigment particle incorporated in the structure of the microcapsule.

As previously mentioned, the microcapsules are activated by driving the core material, e.g., a water-immiscible oily material, from the pigmented precursor microcapsules thereby replacing the oily material with air. By "water-immiscible oily materials," as employed herein, is meant lipophilic materials which are preferably liquid, such as oils, which will not mix with water and which can be driven through the porous, solid walls of the particular precursor microcapsules employed. The discrete precursor-microcapsules of the present invention may be prepared using low melting fats and waxes as the lipophilic material. However, oils are the preferred core material, since they do not require special temperature maintenance during the production of the microcapsules. Furthermore, oils are more easily volatilized and driven through the micropores of the walls of the microcapsules by the application of heat.

In general, the lipophilic nucleus material may be a natural or synthetic oil, fat or wax or any mixture thereof which can be removed from the microcapsules at the desired temperatures. Among the materials that can be employed in the process of the present invention are: mineral spirits, natural oils such as castor oil, soyabean oil, petroleum lubricating oils, fish liver oils, and essential oils, such as methyl salicylate, halogenated biphenyls and low melting fats and waxes.

The preferred lipophilic material for employment in the present invention are those oils having a fairly high vapor pressure (high volatility), so that it can be completely and easily expelled through the micropores of the solid-walled microcapsules by the application of moderate amounts of heat. It is preferred to employ oils that can be expelled from the capsule walls at temperatures between 25° and 200°C., preferably between 80° and 125°C. It is especially preferred, for example, to employ oils which can be driven from the microcapsules at temperatures conventionally employed in the drying of paper webs or paper coatings, e.g., about 85°C. Preferred oils for use in the present invention include mineral spirits, chlorinated biphenyls, xylene, toluene, styrene, turpentine, and oils having a like volatility.

The colloidal emulsifying agents which may be used in the formation of the precursor microcapsules are "amphiphilic." That is, while the emulsifiers are generally preferentially soluble in one phase of the emulsion, they do possess an appreciable affinity for the other phase. It can be said, then, that an amphiphilic emulsifier gives oil a more hydrophilic nature than it had before and, conversely, gives water a more lipophilic nature. Exemplary of the amphiphilic colloidal emulsifying agents which can be used in the present invention are: naturally-occurring, lyophilic colloids including gums, proteins and polysaccharides, such as gum arabic, gum tragacanth, agar, gelatin and starch; and synthetic materials such as hydroxyethyl cellulose, methyl cellulose, polyvinyl pyrrolidone, copolymers of methyl vinyl ether and maleic anhydride and polyvinyl alcohol.

The thermoplastic resins which may function as the encapsulating materials must be of a hydrophobic nature. In other words, they should not be capable of dissolving readily in water. While it is true that all resins exhibit some, even though very small hydrophilic properties, those resins acceptable for use in this aspect of the invention must for the most part be hydrophobic, that is, more lipophilic than hydrophilic.

In general, the thermoplastic resins are macromolecular polymers, copolymers or block polymers. The preferred resins are those containing non-ionizable groups, since the extent to which a resin ionizes has an ultimate effect on the resin's hydrophilic-hydrophobic properties. Resins such as polyvinyl chloride and polystyrene are non-ionizable and are, therefore, preferred. However, other resins which can be used are polyvinyl acetate, vinyl chloride-vinylidene chloride copolymers, cellulose acetate and ethyl cellulose. Novolak resins which are linear, thermoplastic condensation products of phenol and formaldehyde, are also capable of being used as the thermoplastic resin. The novalaks are permanently fusible and soluble as long as their molecular structure is linear.

The selection of solvents for the resin to be used will depend on the specific encapsulating thermoplastic resin and the oil employed. Furthermore, the solvent must be sufficiently miscible with water in order for the resin to

be separated from its solution when the oil-resin mixture is admixed with water.

In general, the solvents which are preferable are organic and of low polarity. Tetrahydrofuran has been used successfully with all of the resins heretofore mentioned and is, therefore, preferred. Examples of other solvents which are suitable include dioxane, cyclohexanone, methyl tetrahydrofuran, methyl isobutyl ketone and acetone.

A small amount of stabilizer may be incorporated with the solution of the thermoplastic resin to increase the stability of the resin towards heat, light and aunospheric oxygen. Examples of stabilibers which may be used include dibasic lead phosphite, dibasic lead stearate, tribasic lead sulfate, monohydrate and dibutyltin maleate. The use of such stabilizers for stabilizing thermoplastic resins is conventional.

The partially condensed thermosetting resinous polymers which may be used in various embodiments of this invention must also be of a hydrophobic nature in their solid, infusible state. These polymers comprise that broad class of compositions known as formaldehyde condensation products and include condensation reaction products of formaldehyde with phenols, such as hydroxybenzene (phenhol), metacresol and 3,5 - xylenol; carbamides, such as urea; triazines, such as melamine; amino and amido compounds, such as aniline, p - toluene - sulfonamide, ethyleneurea and guanidine; etones, such as acetone and cyclohexanone; aromatic hydrocarbons, such as naphthalene; and heterocyclic compounds, such as thiophene. Under the influence of heat, these resins change irreversibly from a fusible and/or soluble material into an infusible and insoluble material.

The preferred formaldehyde condensation products employed in this invention are partially - condensed melamine - formaldehyde, phenol - formaldehyde and urea formaldehyde reaction products. These partially condensed reaction products can be prepared easily according to conventional practices. For example, a melamine-formaldehyde partial condensate or syrup, which may be used as an encapsulating agent, is prepared by refluxing 125 grams of melamine in 184 milliliters of formalin (37% by weight of formaldehyde) neutralized to a pH of 8 with sodium carbonate. The mole ratio of formaldehyde to melamine in this reaction mixture is 2.3 to 1. The reaction continues for about 1 to 1.5 hours at a temperature between 92° and 96°C. or until 1 volume of the condensate becomes turbid when diluted with 2 to 10 volumes of water. The condensate can be used immediately or can be stored for later use by adding a small amount, about 6 to 15% by weight, of methanol to the condensate. The methanol prevents any further rapid condensation of the condensate solution upon standing and can be evaporated from the syrup either prior to or during the admixing operation. The resinous condensate or syrup, either with or without methanol, defines an aqueous solution of a partially condensed, highly cross-linkable resinous polymer, said solution being capable of being diluted up to at least twice its volume before any appreciable separation of the polymer from its solution occurs. After separation of the polymer from its solution, the condensation reaction continues with time to effect additional cross-linking of the partially condensed materials. This additional condensation or cross-linking may be accelerated by the application of heat to the precipitated particles or by the addition of an acidic catalyst, such as HCl or NH_4Cl. Additionally, microcapsules comprising walls of a thermosetting resin material become harder with the passage of time. However, an inhibitor, such as sodium or ammonium hydroxide may be added to stop the curing of the resinous material when the desired hardness is obtained.

Preferably, a small amount of a stabilizer is added to the thermosetting resin syrup in order to improve the stability of the resin towards heat, light and oxygen. For example, from about 0.3 to 0.5% by weight of a conventional stabilizer such as zinc stearate or dibasic lead stearate may be used.

As previously mentioned, the dilution of either one or both of the resinous polymer solutions should take place as the final operation of the process, which dilution takes place slowly and under conditions of brisk agitation. In other words, the sequence of admixing the ingredients may generally proceed in any order so long as the separation or precipitation of a resin from solution results in the encapsulation of oil droplets. Thus, when a single resin is to be used, the order of addition must be such that either water or the resin solution is the last addition.

Brisk agitation is required in order to obtain very small droplets of the emulsion and, ultimately, very small capsules. As previously mentioned, microcapsules having average particle diameters ranging from below about one micron are preferred, with between about 0.25 and about 0.8 micron being especially preferred according to the practice of this invention. Agitation should be conducted in such a manner that when preparing the microcapsules, the emulsion droplets have a predetermined average diameter. Preferably, the emulsion droplets are provided with an average diameter of between 0.25 and 0.8 micron prior to encapsulation, so that upon completion of encapsulation the average final particle diameter is between 0.8 and 1.0 micron. Agitation may be achieved by means of a high speed mixer or impeller, by ultrasonic waves or by other conventional means. Brisk agitation need be maintained only in the

zone of admixing and not throughout the entire volume of the liquid to which the outer liquid is being added.

Regardless of the manner in which the pigment and oil-containing precursor microcapsules are prepared, the microcapsules are heated to temperatures which cause the oil, fat or wax to volatilize and pass through the micropores in the solid walls of the microcapsules. The heating of the precursor microcapsules may take place at any time subsequent to their formation. In the case of the pigmented microcapsular opacifiers to be used on fibrous substrates, the oily material may be driven from the microcapsules either before or subsequent to their being coated onto the substrate. For example, a dispersion of the oil-containing microcapsules may be spray-dried so as to provide air-containing microcapsules, which be then be coated onto the substrate.

The pigment-containing precursor microcapsules may contain a water-miscible core material. For example, if the oily material is driven from the suspended microcapsules prior to their being coated onto or incorporated into a substrate or a surface finish, the oily material may be replaced by another liquid such as water or whatever other liquid may constitute the medium in which the microcapsules are suspended. Likewise, a dispersion of the microcapsules having a water-miscible core material may be spray-dried to provide the air-containing microcapsules of the present invention.

The invention will now be described with reference to the accompanying drawings which, apart from Figure 10 are flow sheets.

Referring now to the drawings, Figure 1 is a flow sheet which illustrates the various alternative modes of producing a substrate coated with the microcapsular opacifiers of the present invention.

In the encapsulating process shown in Figure 1, an oily material such as a chlorinated biphenyl is provided for the microcapsular core. This material is admixed with an aqueous solution of an emulsifying agent, e.g., methyl cellulose, and a finely divided inorganic pigment, e.g., titania. The oily material and the aqueous pigment-containing admixture is agitated until emulsion droplets having an average diameter of a predetermined size, e.g., less than one micron, are produced. Next, an aqueous solution of an encapsulating agent, e.g., a urea-formaldehyde condensation product, is added to the emulsion with brisk agitation, and solid-walled microcapsules are immediately formed. Solid-walled microcapsules thereby become invested with at least one emulsion droplet and an inorganic pigment particle is provided in the microcapsular structure. As previously mentioned, the pigment may be supplied to the system in admixture with the oily material, a solution of the encapsulating agent or with the emulsifying agent as illustrated.

The microcapsules may be optionally cured, e.g., by the addition of glyoxal or other curing agent, and then any one of various procedures may be followed to render the microcapsules useful as opacifying agents. Thus, the microcapsular dispersion may be activated by heating to a temperature of, for example, between about 25° and about 200°C., preferably between about 80° and about 180°C., to volatilise the oily material through the micropores of the capsule walls, for example, the capsules may be spray-dried at 125°C. Next, the microcapsular opacifiers may be admixed with a binder and coated into a substrate and dried. Any suitable temperatures may be employed to volatilise the oily material from the microcapsules, so long the microcapsular structure is not destroyed.

Alternatively, microcapsular opacifiers may be added to a dispersion containing a binder and cellulose fibers. The resulting admixture of the opacifiers and fibers may be formed into a web and dried.

Still another alternative is to coat pigmented oil-containing precursor microcapsules onto a substrate, e.g., a fibrous web, and then heat the microcapsules to drive the oil therefrom.

In the case of surface finishes, such as paints, the volatilizable core material may be volatilised from the pigmentized, air-containing microcapsules either prior or subsequent to their incorporation into the paint as opacifiers.

Figure 2 illustrates a process for the formation of pigmented precursor microcapsules in which an oil-in-water emulsion is encapsulated by a thermoplastic resinous polymer. The resin, in the form of a solution, in which finely divided inorganic pigment is provided, is admixed slowly with the emulsion. However, the admixture may alternatively involve the addition of the emulsion to the resin solution. In either case, the thermoplastic polymer separates from its original solution as minute, solid-walled pigmentized particles by reason of the dilution of the resin solution by the water of the emulsion. Each of the solid-walled particles may contain one or more oil-in-water emulsion droplets in addition to a pigment particle. It should be noted that the polymer should not have appreciable solubility in the core material.

On completion of the dilution operation, the admixture constitutes the minute resin, pigment-containing particles (each containing a droplet(s) of the emulsion) evenly dispersed in an aqueous medium comprising water, the solvent for the resin and residual emulsifying agent. Essentially all of the oily material (in emulsion form) is contained within the resin particles. The thus formed microcapsular dispersion may be heated to volatilise the oil or

may be coated directly onto a web material and heated to produce a coating of opacifiers. As an optional step, a small amount of a binder material may be added to the microcapsular dispersion prior to coating. Such addition aids in binding the microcapsules to the web material.

Figures 3 and 4 illustrate two alternative processes of the microencapsulation of a pigmented oil-in-water emulsion with a thermosetting resin. In Figure 3, the process shown is substantially the same as that shown in Figure 2 with the exception that a partially condensed, aqueous, thermosetting resinous polymer, syrup is substituted for the thermoplastic polymer solution. Although not shown in Figure 3, the optional step of adding a binder material to the microcapsular dispersion prior to coating may be performed.

The process illustrated in Figure 4 involves first preparing a water-in-oil emulsion by admixing the oil material with an amphiphilic emulsifying agent and a thermosetting resinous polymer syrup containing pigment particles. By slowly admixing water with this emulsion, the emulsion will gradually invert to an oil-in-water emulsion. The dilution of the initial emulsion with water simultaneously induces precipitation of the thermosetting resin, thereby encapsulating the oil-in-water emulsion and pigment particles within the precipitated resin particles. The resulting microcapsules, which are evenly dispersed throughout an aqueous medium containing a residual emulsifying agent, may then be coated onto a web material and dried to drive off the oil or, alternatively, an additional amount of a binder may be admixed with the dispersion prior to coating, such as shown in Figure 2.

Figures 5, 6 and 7 illustrate three alternative processses for the microencapsulation of the oil-in-water emulsion and the provision of pigments in the microcapsular structures involving both a thermoplastic and a thermosetting polymer. In Figure 5, a process is shown which may be considered a modification of the process shown in Figure 4. More specifically, the sequence of admixing in the Figure 5 process is identical to that of Figure 4, except that a solution of a thermoplastic resin in a water- and oil-miscible solvent is added to the initial emulsion prior to dilution with water. On subsequent dilution the emulsion inverts and the polymers precipitate to encapsulate the emulsion droplets and provide pigment particles in the microcapsular structure.

Both Figures 6 and 7 illustrate the formation of microcapsules wherein the initial microencapsulation of the oil-in-water emulsions takes the form of the processes shown in Figures 4 and 2, respectively. Thus, in the process of Figure 6, a thermoplastic resinous polymer solution containing pigment particles is admixed with the aqueous dispersion of thermosetting resin microcapsules produced according to the process of Figure 4. The water which is present in the dispersion effects a dilution of the thermoplastic polymer solution, which dilution induces the precipitation of the thermoplastic polymer. Essentially all of the perviously formed thermosetting resin microcapsules are, thereby, encapsulated by the newly precipitated thermoplastic resin. In addition, some of the residual emulsifying agent in the dispersion medium is caused to be entrapped within thet thermoplastic resin microcapsules.

Similarly, in the process of Figure 7, a partially condensed, aqueous, thermosetting resinous polymer syrup containing pigment particles is admixed with the aqueous dispersion of thermoplastic polymer microcapsules produced according to the process of Figure 2. The water in the dispersion causes the precipitation of the thermosetting polymer, thus encapsulating the dispersed pigmented, thermoplastic polymer microcapsules.

Regardless of the method employed for forming the pigmented precursor microcapsules, the microcapsules may be heated so as to obtain an air-containing core, in the manner previously described.

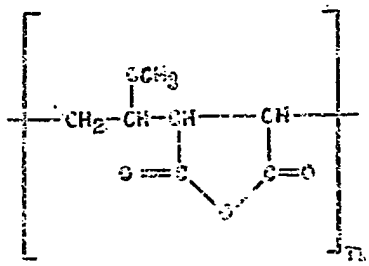
The substrate employed in the present invention may be either a fibrous substrate, such as paper, a non-fibrous substrate, such as a film, or a surface finish, such as paint. However, the microcapsules such as those produced by the herein disclosed processes are also capable of being coated onto other fibrous substrates, such as plastic and fabric or textile webs.

Generally, there is sufficient residual emulsifying agent remaining in the microcapsular dispersion after separation of the resin and encapsulation of the emulsion that no additional binding agent need be used if the capsules are to be applied to a fibrous substrate. Materials such as gelatin and gum arabic have been used conventionally as binding agents. However, it is preferable to add an additional binder such as hydroxyethyl cellulose, methyl cellulose or starch to the system.

According to still another process for forming the pigmented, oil-containing precursor microcapsules, a primary oil-in-water emulsion is formed, which emulsion comprises the water-immiscible oil, fat or wax previously described and pigment particles. The oily material is dispersed in the form of microscopic droplets in a colloidal solution of one or more colloidal emulsifying agents. At least one of the said emulsifying agents must possess groups capable of reacting with a cross-linking or complexing agent to form a capsule wall around said dispersed microscopic droplet. The cross-linking or complexing agent is slowly added to the emulsion with brisk agitation, and this is continued until the final microcapsules are formed having substantially con-

tinuous solid walls, as hereinabove defined. The emulsion containing the precursor microcapsules may be heated to produce the opacifiers or may be directly coated onto a web material as previously described. Alternatively, the microcapsules may be separated from the emulsion by physical means, such as filtration, centrifugation, or spray drying. Subsequently, the microcapsules may be redispersed in a solution of a binder and coated onto a web material or may be dispersed in a non-fibrous substrate.

The encapsulating material used in this process may also be an emulsifying agent which is self-complexing or self-cross-linking. In such a case, the addition of another cross-linking or complexing agent is unnecessary. Exemplary of emulsifying agents having the aforesaid characteristics which permit their employment are: naturally-occurring colloids including gums, proteins and polysaccharides, such as gum tragacanth, guar gums and gelatin; and synthetic materials such as polyvinyl alcohol and copolymers of methyl vinyl ether and maleic anhydride. Suitable copolymers of methyl vinyl ether and maleic anhydride are commercially available under the trademark "Gantrez." These water-soluble copolymers have the general structure



in which n is an integer. The above list comprises both gellable and non-gellable emulsifying agent, e.g., gelatin (gellable) and polyvinyl alcohol (non-gellable). Emulsifying agents which are self-cross-linking or self-complexing include certain derivatives of guar gum, such as those which are commercially available under the trademark "Jaguar." These materials are natural hydrophilic colloids that are produced by the extraction of guar gum from the endosperm portion of cyamopsis tetragonalobus seeds and are comprised of a straight chain galacto mannan polysaccharide made of many mannose and galactose units linked together.

The crosslinking or complexing agents employed with the aforesaid emulsifying agents belong to three broad categories: (1) monomeric organic compounds, such as the aldehydes, e.g., formaldehyde, glyoxal and other formaldehyde donors, trioxane ethanolamine, and ethylene diamine; (2) ordinary inorganic compounds, such as sodium borate and boric acid; and (3) macromolecular species, such as gelatin, gum tragacanth, and methylcellulose.

While some of the cross-linking or complexing agents are suitable for use with a plurality of emulsifying agents, others are not. Thus, the preferred cross-linking or complexing agent-emulsifying agent pairs include: (1) gelatin with an aldehyde, such as formaldehyde; (2) polyvinyl alcohol with sodium borate; (3) copolymers of methyl vinyl ether and maleic anhydride with any one of gelatin, gum tragacanth, ethanolamine, ethylene diamine, polyvinyl alcohol; (4) guar gum derivatives with either of sodium borate or methylcellulose; and (5) self-complexing guar gum derivatives with themselves.

The cross-linking or complexing agent is utilized in amounts sufficient to result in the formation of microcapsules. The relative amounts vary with the particular system, and may be easily determined in each case.

Figures 8 and 9 of the attached drawings illustrate the processes for the production of pigmented precursor microcapsules mentioned above. In the process shown in the flow sheet of Figure 8, a primary oil-in-water emulsion containing inorganic pigment is prepared by dissolving the emulsifying agent or combination of agents and pigment particles in the oily material and subsequently adding water to emulsify.

The water may be added to the emulsifying agent-oil mixture either quickly or slowly with agitation. If the water is added slowly to the oil phase containing the emulsifying agent or agents, a water-in-oil emulsion is formed, which is eventually inverted to an oil-in-water emulsion with the further addition of water. Such an inversion step results in a more stable emulsion with some systems, e.g., a methyl cellulose-guar gum derivative system.

The temperature of emulsification may be varied over a broad range. However, the temperature must be kept above the gelling point of the emulsifying agent or agent only if a gelable emulsifying agent is used. Therefore, when a non-gelable emulsifying agent is used, e.g., polyvinyl alcohol, the temperature during emulsification can be varied appreciably without altering the final desired results.

Subsequent to the emulsification process, the cross-linking or complexing agent is added to the oil-in-water emulsion, slowly, and with brisk agitation to form the precursor microcapsules. Agitation may be achieved by means of a high speed mixer or impeller, by ultrasonic waves or by other conventional means so long as microcapsules having an average particle size of less than two microns are formed.

If the emulsifying agent is of the self-complexing variety, e.g., a self-complexing guar gum derivative, the cross-linking or com-

plexing agent comprises the same material as the emulsifying agent.

Alternatively, the emulsion containing the microcapsules may be either coated directly onto a web material and dried or the microcapsules may be separated from the emulsion by some physical means such as filtration, spray drying centrifugation; redispersed in a solution of a binder; coated onto a web material and dried. Removal of the oil from the interior of the capsule may be done either before or after coating, as before. Suitable binders include methyl cellulose, starch, casein, polyvinyl alcohol, synthetic latex, and styrene-butadiene rubber. Alternatively, materials such as urea-formaldehyde or melamine-formaldehyde condensates may be employed.

In the encapsulation process illustrated in Figure 9, the oil-in-water emulsion is prepared by admixing pigment particles and the emulsifying agent (or agents) with water and subsequently adding the oily material to the water solution with agitation until complete emulsification has occurred. The emulsion may then be diluted with water to give the desired viscosity suitable for coating. Capsule diameters suitable for producing the microcapsular opacifiers of the present invention are likewise obtainable by the process of Figure 8 by adding cross-linking or complexing agents with agitation as previously described.

Figure 10 represents a cross-sectional view of a portion of a fibrous substrate produced according to a procedure of the present invention wherein a paper web material 10 contains a substantially uniform coating of pigmented, air-containing opacifiers 12 having a predetermined average diameter. The binding agent employed to secure the opacifiers to the paper web is not shown.

The following examples illustrate the production of pigmented, air-containing microcapsular opacifiers and constitute the best modes contemplated for carrying out the present invention. The ream of paper as employed in the following examples comprises 500 sheets of 25 inch by 38 inch paper or a total of 3300 square feet of paper. Likewise, the paper employed in the following examples is bond paper (32.5 pounds per ream) having a TAPPI opacity of 73 percent points prior to coating. The titanium dioxide pigment employed in the following examples has a particle diameter in the range of 0.1 to 0.35 micron.

Example 1

Six grams of titania, are dispersed in 366 grams of an 8.2% (by weight) methyl cellulose (15 centipoises) solution in water. Into the above dispersion, 200 grams of mineral spirits are emulsified in a blender. Emulsification is continued until the average particle diameter of the emulsion droplets is about 0.8 micron. Subsequently, 90 grams of an aqueous B-stage urea-formaldehyde condensate (65% by weight solids) are slowly added to the emulsion with continued agitation in order to induce encapsulation. Pigment and oil-containing precursor microcapsules thereby are formed.

The pigment and oil-containing microcapsules are coated onto a web comprising bond paper. The bond paper is coated with 5.42 pounds per ream of pigment and oil-containing precursor microcapsules. The paper web is dried at a temperature of about 85°C. for a period of time sufficient to drive-off the mineral spirits and produce the air-containing microcapsules, viz., 15 minutes. These microcapsules have an unexpectedly high TAPPI opacity of 92.2% points. (This corresponds to a 19.1% points increase in the opacity of the uncoated paper.) The weight of the paper web is only increased to the extent of 4.5 pounds per ream of paper.

An equivalent amount of titania *per se* (4.5 pounds per ream) is coated on the same paper. The corresponding increase in TAPPI opacity is only 14.10% points, as compared with the 19.1% points increase employing the pigment and air-containing opacifiers of the present invention.

Example 2

Titanium dioxide in an amount of 10.5 grams is dispersed in 366 grams of an 8.2% (by weight) of a (15 centipoises) methyl cellulose solution in water, emulsified with 150 grams of mineral spirits and encapsulated with 40 grams of a B-stage ureaformaldehyde (65% solids) solution.

The average capsule diameter is about 0.8 micron. The pigment and oil-containing microcapsules are coated on bond paper and heated at 85°C. to remove the mineral spirits. A final coating weight of 4.2 pounds per ream of the pigment and air-containing microcapsules results in a 16.9% points increase in the TAPPI opacity of the paper. An equivalent coat weight (4.1 pounds per ream) of titania gives a corresponding increase in opacity of only 13.25% points.

Example 3

The procedure of Example 2 is repeated except that 20 grams of titania are employed and the emulsifier, ureaformaldehyde, is employed in the amount of 60 grams. The average particle diameter of the capsules is 0.8 micron. A coating weight of 4.0 pounds per ream of the pigment and air-containing microcapsules results in a 19.61% points increase in the TAPPI opacity of the base paper. An equivalent amount (4.0 pounds per ream) of titania yields only a corresponding increase in opacity of 13.05% points.

Example 4

The procedure of Example 3 is repeated except that 30 grams of titania, 200 grams of mineral spirits and 90 grams of urea-

formaldehyde are employed in the formation of the pigmented, air-containing microcapsules. The average particle diameter of the microcapsules is 1.3 microns.

A coating weight of 4.0 pounds per ream of air-containing microcapsules results in an increase in TAPPI opacity of the base paper of 16% points. The corresponding increase in opacity for an equivalent amount (4.0 pounds per ream) of titania is 13.05% points.

EXAMPLE 5

Again, the procedure of Example 3 is repeated, except that 2.5 grams of titania and 10 grams of urea-formaldehyde are utilized in the preparation of the precursor microcapsules. The average particle diameter of the resulting pigmented, air-containing microcapsules is a preferred 0.8 micron.

A coating weight of 4.9 pounds per ream of air-containing microcapsules yields an increase in the opacity of the base paper of 18.5% points, whereas the same coating weight of TiO_2 results in only a 14.9% increase in opacity.

EXAMPLE 6

Six grams of calcium carbonate having a particle size of 0.9 micron are dispersed in 366 grams of an 8.2% (by weight) methyl cellulose (15 centipoises) solution in water. The resulting dispersion is emulsified with 200 grams of mineral spirits and there is then slowly added to the emulsion 90 grams of B-stage urea-formaldehyde (65% solids) solution whilst maintaining conditions of agitation. The average particle diameter of the resulting emulsion is 1.0 micron. The resulting dispersion of pigment and oil-containing microcapsules is then coated on to a web comprising bond paper in the manner described in Example 1. A coating weight of 5.5 pounds per ream of the pigment and air-containing microcapsules results in an increase of 16.0% points in TAPPI opacity of the base paper.

When an equivalent amount of calcium carbonate (5.5 pounds per ream) is coated on the same paper, the corresponding increase in TAPPI opacity is only 10.8% points.

EXAMPLE 7

The procedure of Example 6 is repeated using 6 grams of zinc oxide pigment having a particle size of 0.12 micron instead of calcium carbonate. A resulting coating weight of 4.7 pounds per ream of the air-containing microcapsules yields an increase in the TAPPI opacity of the base paper of 15.6% points. An equivalent coat weight (4.7 pounds per ream) of zinc oxide pigment, *per se*, on the same base paper gives a corresponding increase in opacity of only 7.5% points.

EXAMPLE 8

Example 6 is repeated using 6 grams of clay (Ultrawhite-90) having a particle size of 2.0 microns instead of calcium carbonate. A resulting coating weight of 7.3 pounds per ream of pigment and air-containing microcapsules gives an increase in the TAPPI opacity of the base paper of 19.1% points as compared to an increase of only 8.5% points of an equivalent coat weight (7.3 pounds per ream) of the clay above on the same base paper.

EXAMPLE 9

Example 6 is repeated using 6 grams of barium sulphate having a particle diameter of 0.25 micron, insted of calcium carbonate. A resulting coat weight of 7.1 pounds per ream of the pigment and air-containing microcapsules gives in increase in the TAPPI opacity of the base paper of 18.9% points. An equivalent coating weight (7.1 pounds per ream) barium sulphate on the same base paper yields a corresponding increase in opacity of only 3.9% points.

EXAMPLE 10

Example 6 is repeated with the exception that 6 grams of alumina trihydrate having a particle diameter of 0.67 micron are employed instead of calcium carbonate. A resulting coat weight of 5.9 pounds per ream of the pigment and air-containing microcapsules gives an increase in the TAPPI opacity of the base paper of 17.3% points. An equivalent coating weight of the alumina pigment on the same base paper yields a corresponding increase in opacity of only 12.8 points.

EXAMPLE 11

Titanium dioxide in an amount of 2 grams is dispersed in 366 grams of an 8.2% (by weight) of a 15 centipoises methyl cellulose solution in water, emulsified with 150 grams of mineral spirits and encapsulated with 90 grams of a B-stage urea-formaldehyde (65% by weight) solution in water. The average microcapsule diameter is 0.8 micron. To the microcapsular dispersion 10.0 grams of a 30% by weight citric acid solution in water are added and the dispersion is cured at 35°C. for 30 minutes.

The cured microcapsules are coated onto bond paper and dried at 85°C. to remove the mineral spirits. A coating weight of 7.4 pounds per ream of the air-containing microcapsules results in an increase in the TAPPI opacity of the base paper of 19.4% points. The corresponding increase in opacity for an equivalent coat weight of titania pigment, *per se*, is only 18.6% points.

EXAMPLE 12

One hundred grams of mineral spirits are emulsified with 188 grams of an 8.2% by weight methyl cellulose solution in water. Three grams of titania are dispersed in 45 grams of a urea-formaldehyde (65% by weight) solution in water and added slowly to

the above emulsion. The average particle diameter is 0.8 micron.

The microcapsular dispersion is coated onto bond paper and heated at 85°C. to drive-off mineral spirits. A coating weight of 6.9 pounds per ream of the pigment and air-containing microcapsules results in an increase in TAPPI opacity of the base paper of 18.9% points. An equivalent coating weight of titania yields a corresponding increase in TAPPI opacity of 18.1% points.

EXAMPLE 13

Three grams of titania are dispersed in 100 grams of mineral spirits. To this mixture, 15 grams of (15 centipoises) methyl cellulose and 203.0 grams of water are added and emulsified for 15 minutes. To the emulsion, 45 grams of a (65% by weight) urea-formaldehyde solution in water are added.

The average microcapsule diameter is 1.7 micron. The microcapsular dispersion is coated onto bond paper and heated at 85°C. to remove the mineral spirits. A coating weight of 4.66 pounds per ream of the air-containing microcapsules yields an increase in the TAPPI opacity of the base paper of 15.0% points. An equivalent coating weight of titania *per se*, results in a 14.4% points increase in opacity.

The opacifiers of the present invention may be employed in all known applications where conventional opacifying pigments have been used for inducing or increasing opacity. For example, the opacifiers may be used in paints, as inks, in plastics, on metals, glass, wood, plaster, in films, on fabrics and on paper. As previously mentioned, expressions such as "microcapsules containing pigments" and "pigmentized microcapsules" are intended to include microcapsules having at least a portion of the pigment particle incorporated in the microcapsular structure.

WHAT WE CLAIM IS:—

1. Pigmented microcapsules comprising discrete, substantially spherical, air-filled microcapsules having substantially continuous organic polymeric solid walls and an average particle diameter of less than 2 microns, said microcapsules also having inorganic pigment particles incorporated in the microcapsular structure.

2. Pigmented microcapsules according to Claim 1 having an average particle diameter of between 0.10 and 1.0 micron.

3. Pigmented microcapsules according to either of Claims 1 or 2 having an average particle diameter of between 0.25 and 0.8 micron.

4. Pigmented microcapsules according to any of Claims 1—3 in which the pigment is titania, barium sulphate, zinc oxide, calcium carbonate or aluminium oxide trihydrate.

5. A method for the production of microcapsules as claimed in any of Claims 1—4 which comprises preparing discrete, substantially spherical, precursor microcapsules pigmented with an inorganic pigment and having substantially continuous organic polymeric solid walls said microcapsules having an average diameter of less than 2 microns and containing a volatilisable liquid core material, and heating said microcapsules in the presence of air to a temperature sufficient to substantially completely valatilise said core material from said microcapsules and replace said core material by air.

6. A method as claimed in Claim 5 wherein said microcapsules have an average particle diameter of between 0.10 and 1.0 micron.

7. A method as claimed in either of Claims 5 or 6 wherein said microcapsules have an average particle diameter of between 0.25 and 0.8 micron.

8. A method according to any of Claims 5—7 wherein said pigment is titania, barium sulphate, zinc oxide, calcium carbonate or aluminium oxide trihydrate.

9. A method according to any of Claims 5—8 wherein said liquid core material is a water-immiscible liquid.

10. A method according to any of Claims 5—9 wherein said liquid core material is a liquid or low melting oil, fat or wax.

11. A method according to any of Claims 5 to 10 wherein said liquid core material is mineral spirits, a liquid chlorinated biphenyl, toluene, styrene or turpentine.

12. A method as claimed in any of Claims 5 to 11 wherein said precursor microcapsules are made by a process which comprises admixing inorganic pigment and

(a) a substantially water-immiscible oily material which is a liquid or low melting oil, fat or wax;

(b) an amphiphilic colloidal emulsifying agent having a group or groups capable of reacting with a crosslinking or complexing agent and which subsequently becomes incorporated into the wall structure of the precursor microcapsules;

(c) at least one solution comprising a resinous polymer, said solution being either

(i) a solution comprising a hydrophobic, thermoplastic resinous polymer which is substantially insoluble in said oil, fat or wax dissolved in a water- and oil-miscible organic solvent, said thermoplastic polymer being capable of separating from said solution in solid particulate form upon dilution with water; or

(ii) a solution comprising a partially condensed thermosetting resinous polymer dissolved in water, said polymer being capable of separating in solid particulate form from said solution upon dilution with more water; or

(iii) a mixture of solutions (i) and (ii); and

(d) sufficient additional water to cause the separation of said thermoplastic polymer and/or said thermosetting resinous polymer from solution (i) and/or solution (ii) the sequence of admixture being such that said thermoplastic and/or said thermosetting polymer separates from solution in solid form about a nucleus of inorganic pigment and at the interface of oil-in-water droplets newly or previously formed and upon gradual addition of said additional water under conditions of brisk agitation.

13. A method as claimed in Claim 12 in which said water-immiscible oily material is mineral spirits, a natural oil, a petroleum lubricating oil, a fish liver oil, an essential oil or a liquid halogenated biphenyl.

14. A method as claimed in either of Claims 12 or 13 in which said colloidal emulsifying agent is a naturally-occurring lyophilic colloid, hydroxyethyl cellulose, methyl cellulose, polyvinylpyrolidone, a copolymer of methyl vinyl ether and maleic anhydride or polyvinyl alcohol.

15. A method according to any of Claims 5 to 11 wherein the precursor microcapsules are produced by a process which comprises:

(a) forming an oil-in-water emulsion of a water-immiscible oily material which is a liquid or low melting oil, fat or wax in an aqueous solution in an aqueous solution of one or more colloidal emulsifying agents which contain groups capable of reacting with a cross-linking or complexing agent, said emulsion also containing inorganic pigment particles; and

(b) slowly adding to said emulsion a cross-linking or a complexing agent which reacts with the groups in said colloidal emulsifying agent or agents so as to form an impermeable coating around the disperse phase of said emulsion under conditions of brisk agitation.

16. A method according to Claims 12 to 14 in which the thermosetting resinous condensation product is a partially condensed urea-formaldehyde, phenol - formaldehyde or melamine-formaldehyde product.

17. A method for the production of air-filled pigmented microcapsules according to Claim 5 and substantially as hereinbefore described with reference to any of the Examples.

18. Air-filled pigmented microcapsules whenever prepared by the process claimed in any of Claims 5 to 17.

19. A method for production of an opaque fibrous substrate which comprises forming a dispersion of discrete, substantially spherical air-filled pigmented microcapsules according to any of Claims 1—4 and coating said dispersion on to a surface of a fibrous substrate.

20. A modification of the method of Claim 19 which comprises coating a dispersion of discrete, substantially spherical, precursor microcapsules having substantially continuous organic polymeric solid walls, said precursor microcapsules being pigmented with an inorganic pigment, having an average particle size of less than 2 microns and containing a volatilisable liquid core material, on to a surface of a fibrous substrate and heating the coated substrate in the presence of air to a temperature sufficient to substantially completely volatilise said liquid core material from said precursor microcapsules.

21. A method according to either of Claims 19 or 20 in which said fibres are cellulosic fibres.

22. A method for the production of an opaque non-fibrous substrate which comprises forming a dispersion of discrete, substantially spherical air-filled pigmented microcapsules according to any of Claims 1—4 and coating said dispersion on to a surface of a non-fibrous substrate.

23. A modification of the method of Claim 22 which comprises coating a dispersion of discrete, substantially spherical precursor microcapsules having substantially continuous organic polymeric solid walls, said precursor microcapsules being pigmented with an inorganic pigment, having an average particle size of less than 2 microns and containing a volatilisable liquid core material, on to a surface of a non-fibrous substrate and heating the coated substrate in the presence of air to a temperature sufficient to substantially completely volatilise said liquid core material from said precursor microcapsules.

24. A method for the production of an opaque fibrous substrate which comprises forming a dispersion of fibres and discrete, substantially spherical precursor microcapsules having substantially continuous organic polymeric solid walls, said precursor microcapsules being pigmented with an inorganic pigment having an average particle size of less than 2 microns and containing a volatilisable liquid core material, forming said dispersion into a fibrous substrate containing said microcapsules and heating said substrate in the presence of air to a temperature sufficient to substantially completely volatilise said volatilisable liquid from said precursor microcapsules.

25. A coating composition which comprises a dispersion of discrete, substantially spherical air-filled pigmented microcapsules according to any of Claims 1—4 dispersed in a vehicle therefor.

26. A non-fibrous substrate having incorporated therein discrete, substantially spherical and-filled pigmented microcapsules according to any of Claims 1—4.

27. A non-fibrous substrate according to Claim 26 in the form of a film.

28. A method for the production of an opaque fibrous substrate according to either of Claims 19 or 20 and substantially as de-

scribed with reference to any of the Examples.

29. A method for the production of an opaque non-fibrous substrate according to either of Claims 22 or 23 and substantially as hereinbefore described.

30. A method for the production of an opaque fibrous substrate according to Claim 24 and substantially as hereinbefore described.

31. An opaque fibrous substrate whenever produced by the process claimed in any of Claims 19, 20 and 28 or 22, 23, and 29.

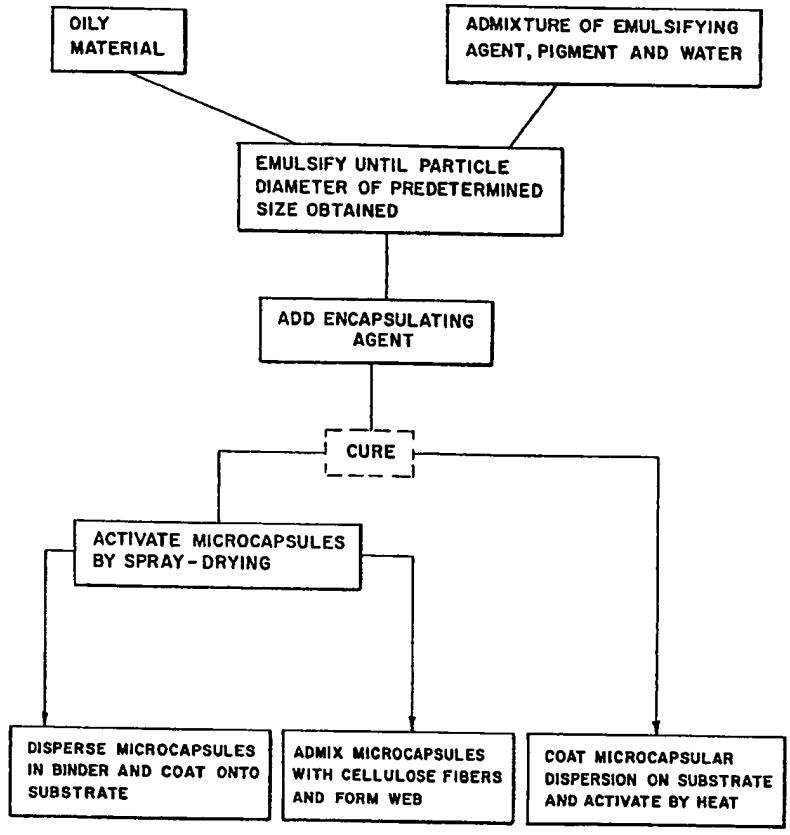
32. An opaque non-fibrous substrate whenever produced by the process claimed in either of Claims 24 or 30.

BARON & WARREN,
16, Kensington Square,
London, W.8.
Chartered Patent Agents.

Printed for Her Majesty's Stationery Office, by the Courier Press, Leamington Spa, 1972.
Published by The Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from which copies may be obtained.

1271463 COMPLETE SPECIFICATION
8 SHEETS *This drawing is a reproduction of the Original on a reduced scale*
Sheet 1

FIG. 1



——— PRINCIPAL STEPS
– – – OPTIONAL STEPS

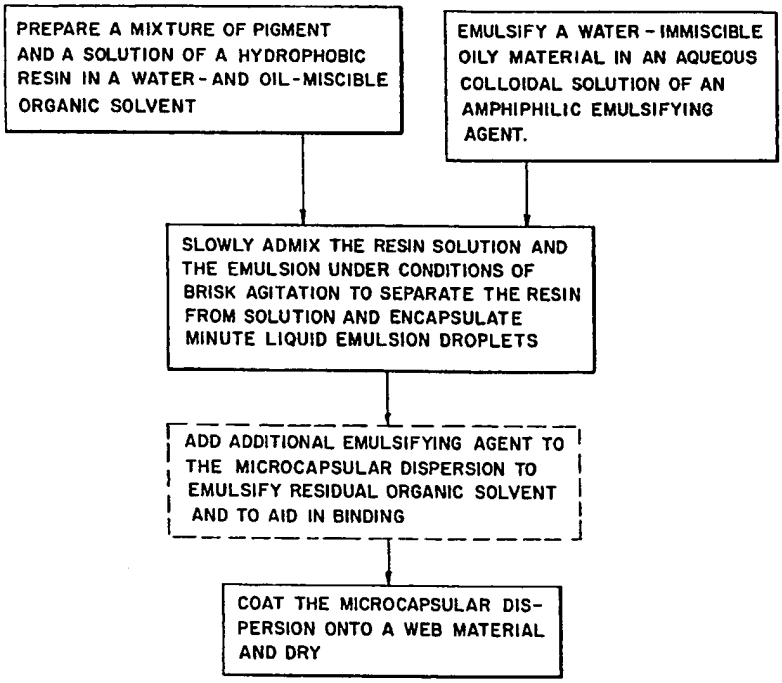

PREPARE A MIXTURE OF PIGMENT AND A SOLUTION OF A HYDROPHOBIC RESIN IN A WATER-AND OIL-MISCIBLE ORGANIC SOLVENT
EMULSIFY A WATER-IMMISCIBLE OILY MATERIAL IN AN AQUEOUS COLLOIDAL SOLUTION OF AN AMPHIPHILIC EMULSIFYING AGENT.
SLOWLY ADMIX THE RESIN SOLUTION AND THE EMULSION UNDER CONDITIONS OF BRISK AGITATION TO SEPARATE THE RESIN FROM SOLUTION AND ENCAPSULATE MINUTE LIQUID EMULSION DROPLETS
ADD ADDITIONAL EMULSIFYING AGENT TO THE MICROCAPSULAR DISPERSION TO EMULSIFY RESIDUAL ORGANIC SOLVENT AND TO AID IN BINDING
COAT THE MICROCAPSULAR DISPERSION ONTO A WEB MATERIAL AND DRY
PRINCIPAL STEPS
OPTIONAL STEPS

FIG. 2

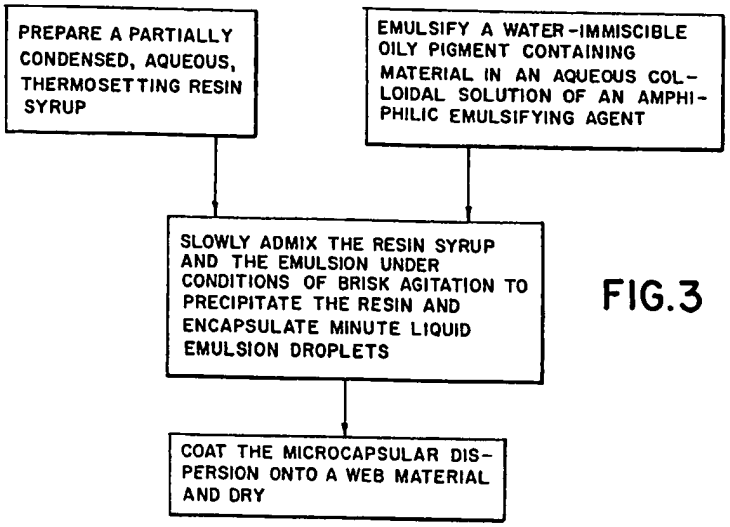

PREPARE A PARTIALLY CONDENSED, AQUEOUS, THERMOSETTING RESIN SYRUP
EMULSIFY A WATER-IMMISCIBLE OILY PIGMENT CONTAINING MATERIAL IN AN AQUEOUS COLLOIDAL SOLUTION OF AN AMPHIPHILIC EMULSIFYING AGENT
SLOWLY ADMIX THE RESIN SYRUP AND THE EMULSION UNDER CONDITIONS OF BRISK AGITATION TO PRECIPITATE THE RESIN AND ENCAPSULATE MINUTE LIQUID EMULSION DROPLETS
COAT THE MICROCAPSULAR DISPERSION ONTO A WEB MATERIAL AND DRY

FIG.3

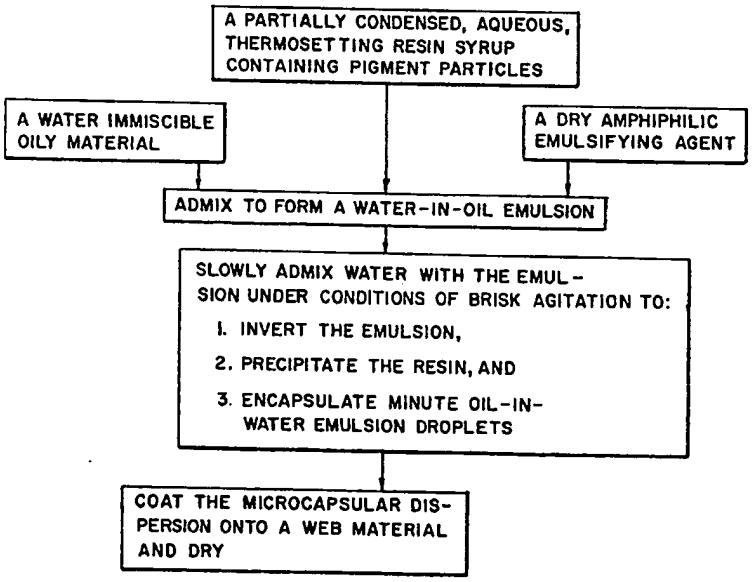

A PARTIALLY CONDENSED, AQUEOUS, THERMOSETTING RESIN SYRUP CONTAINING PIGMENT PARTICLES
A WATER IMMISCIBLE OILY MATERIAL
A DRY AMPHIPHILIC EMULSIFYING AGENT
ADMIX TO FORM A WATER-IN-OIL EMULSION
SLOWLY ADMIX WATER WITH THE EMULSION UNDER CONDITIONS OF BRISK AGITATION TO:
1. INVERT THE EMULSION,
2. PRECIPITATE THE RESIN, AND
3. ENCAPSULATE MINUTE OIL-IN-WATER EMULSION DROPLETS
COAT THE MICROCAPSULAR DISPERSION ONTO A WEB MATERIAL AND DRY

FIG. 4

1271463 COMPLETE SPECIFICATION
8 SHEETS *This drawing is a reproduction of the Original on a reduced scale*
Sheet 4.

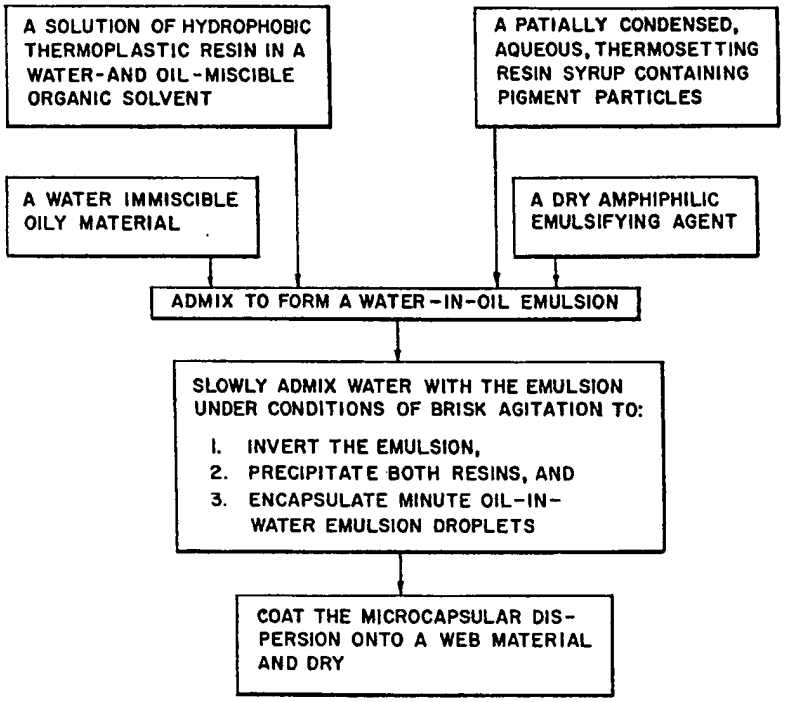


FIG. 5

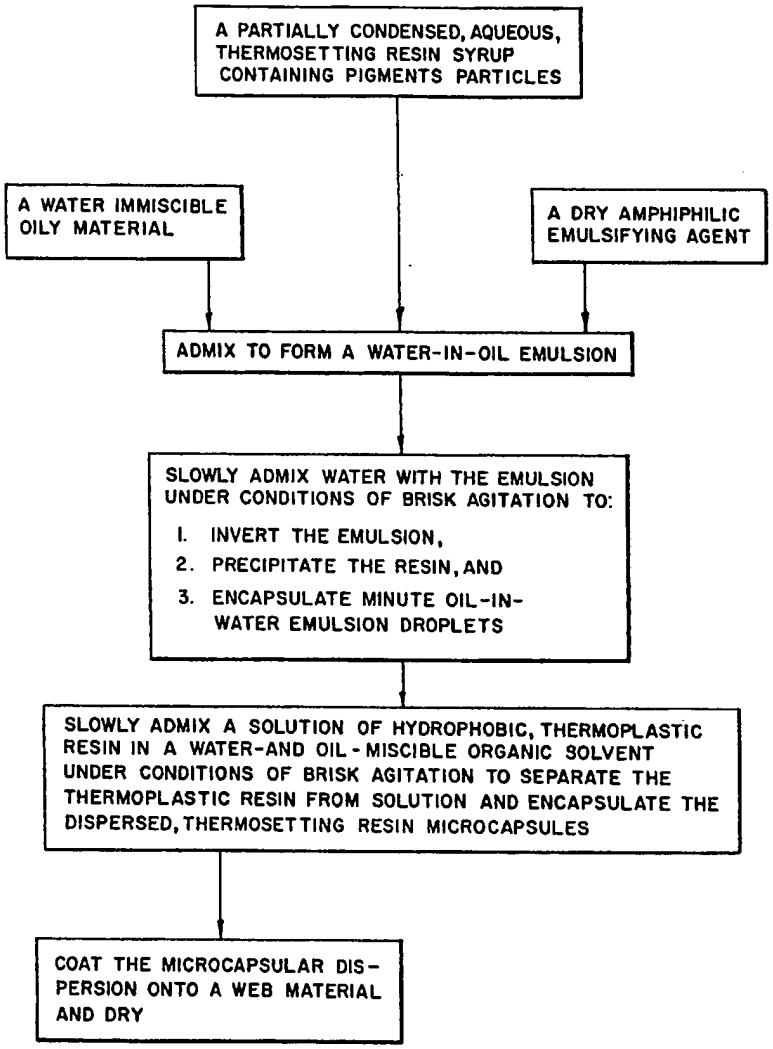

A PARTIALLY CONDENSED, AQUEOUS, THERMOSETTING RESIN SYRUP CONTAINING PIGMENTS PARTICLES
A WATER IMMISCIBLE OILY MATERIAL
A DRY AMPHIPHILIC EMULSIFYING AGENT
ADMIX TO FORM A WATER-IN-OIL EMULSION
SLOWLY ADMIX WATER WITH THE EMULSION UNDER CONDITIONS OF BRISK AGITATION TO:
1. INVERT THE EMULSION,
2. PRECIPITATE THE RESIN, AND
3. ENCAPSULATE MINUTE OIL-IN-WATER EMULSION DROPLETS
SLOWLY ADMIX A SOLUTION OF HYDROPHOBIC, THERMOPLASTIC RESIN IN A WATER-AND OIL-MISCIBLE ORGANIC SOLVENT UNDER CONDITIONS OF BRISK AGITATION TO SEPARATE THE THERMOPLASTIC RESIN FROM SOLUTION AND ENCAPSULATE THE DISPERSED, THERMOSETTING RESIN MICROCAPSULES
COAT THE MICROCAPSULAR DISPERSION ONTO A WEB MATERIAL AND DRY

FIG. 6

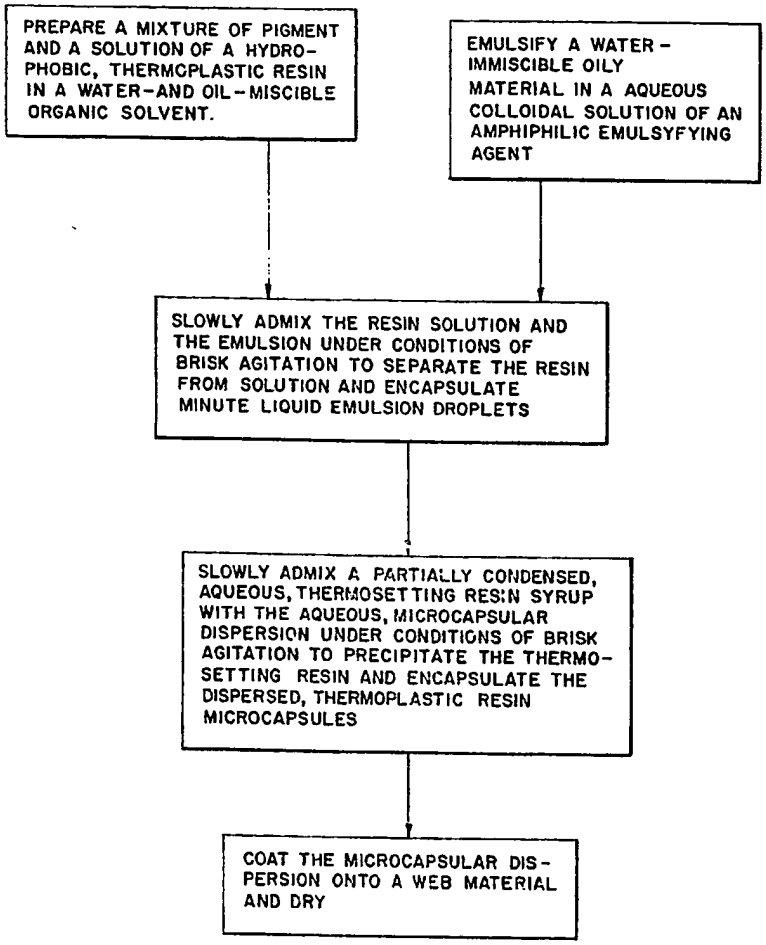

PREPARE A MIXTURE OF PIGMENT AND A SOLUTION OF A HYDROPHOBIC, THERMOPLASTIC RESIN IN A WATER-AND OIL-MISCIBLE ORGANIC SOLVENT.
EMULSIFY A WATER-IMMISCIBLE OILY MATERIAL IN A AQUEOUS COLLOIDAL SOLUTION OF AN AMPHIPHILIC EMULSYFYING AGENT
SLOWLY ADMIX THE RESIN SOLUTION AND THE EMULSION UNDER CONDITIONS OF BRISK AGITATION TO SEPARATE THE RESIN FROM SOLUTION AND ENCAPSULATE MINUTE LIQUID EMULSION DROPLETS
SLOWLY ADMIX A PARTIALLY CONDENSED, AQUEOUS, THERMOSETTING RESIN SYRUP WITH THE AQUEOUS, MICROCAPSULAR DISPERSION UNDER CONDITIONS OF BRISK AGITATION TO PRECIPITATE THE THERMOSETTING RESIN AND ENCAPSULATE THE DISPERSED, THERMOPLASTIC RESIN MICROCAPSULES
COAT THE MICROCAPSULAR DISPERSION ONTO A WEB MATERIAL AND DRY

FIG. 7

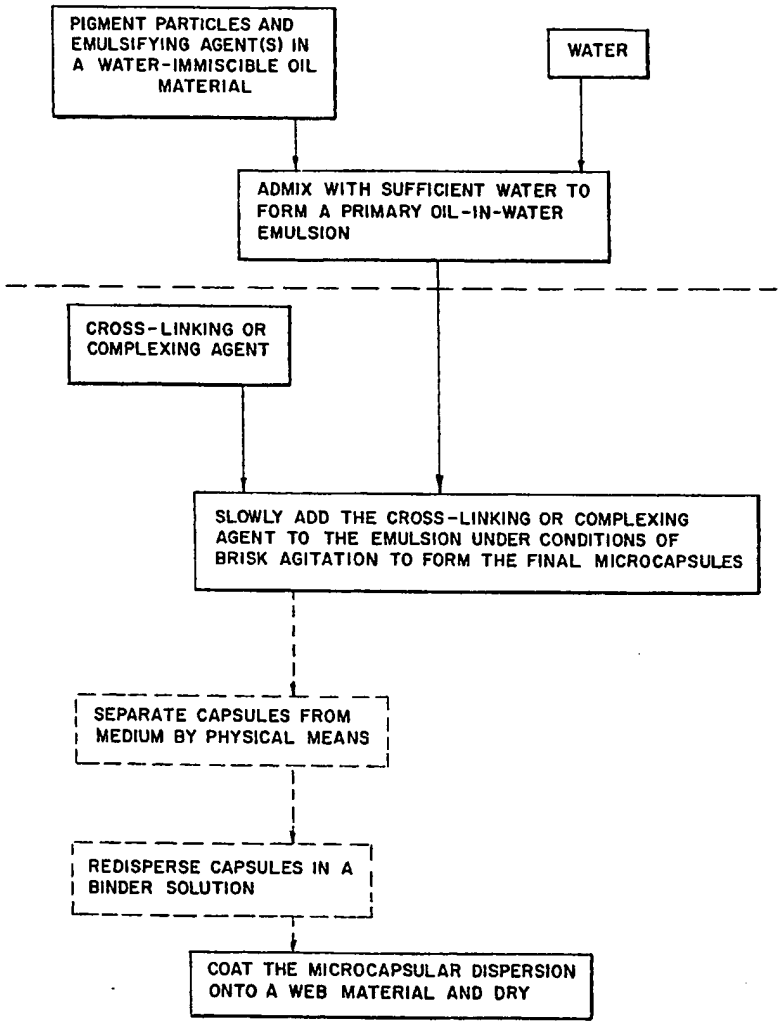

PIGMENT PARTICLES AND EMULSIFYING AGENT(S) IN A WATER-IMMISCIBLE OIL MATERIAL
WATER
ADMIX WITH SUFFICIENT WATER TO FORM A PRIMARY OIL-IN-WATER EMULSION
CROSS-LINKING OR COMPLEXING AGENT
SLOWLY ADD THE CROSS-LINKING OR COMPLEXING AGENT TO THE EMULSION UNDER CONDITIONS OF BRISK AGITATION TO FORM THE FINAL MICROCAPSULES
SEPARATE CAPSULES FROM MEDIUM BY PHYSICAL MEANS
REDISPERSE CAPSULES IN A BINDER SOLUTION
COAT THE MICROCAPSULAR DISPERSION ONTO A WEB MATERIAL AND DRY
PRINCIPAL STEPS
ALTERNATE STEPS

FIG.8

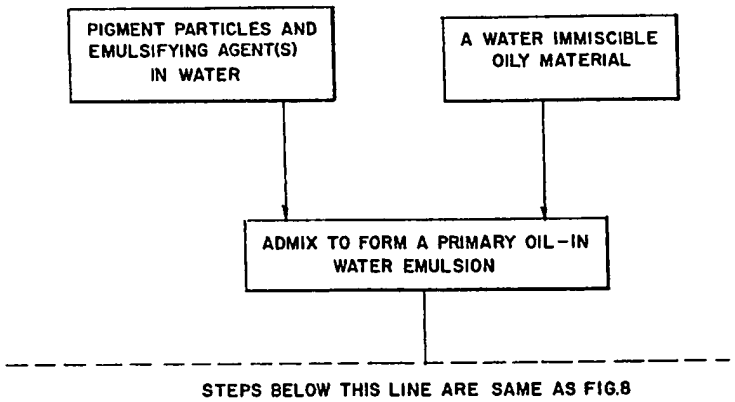

PIGMENT PARTICLES AND EMULSIFYING AGENT(S) IN WATER
A WATER IMMISCIBLE OILY MATERIAL
ADMIX TO FORM A PRIMARY OIL-IN WATER EMULSION
STEPS BELOW THIS LINE ARE SAME AS FIG.8

FIG. 9

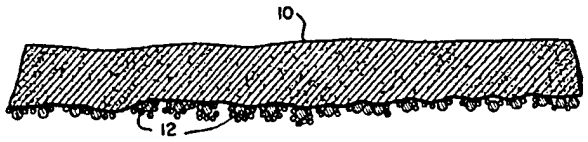

10
12

FIG. 10